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(54) Title: METHOD OF CONVERTING ASBESTOS CEMENT INTO A HARMLESS PRODUCT

(57) Abstract

Asbestos cement may be converted to a harmless product by melting at a melt temperature of 1400 to 1700 °C a blend of 50 to 85 % by weight asbestos cement with 15 to 50 % by weight of additives that include naturally occurring silicate material such that the total blend has a CaO content of not more than 50 %. The melt is discharged from the furnace, cooled and solidified and may be used as aggregate or, generally after solidification as regular units, may be used as part or all of the charge for producing MMV fibre material. It is of particular value for the production of man made vitreous fibre material that has low alumina content and is soluble in lung fluids.

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Method of Converting Asbestos Cement
into a Harmless Product

This invention relates to the conversion of asbestos cement products (which are considered to be harmful because of their content of asbestos fibre) into a harmless product, namely a product that is substantially free of asbestos fibres and so is considered to be inherently much less harmful than the starting asbestos cement product. This harmless product can be, for instance, an aggregate or a product comprising synthetic mineral fibres, which can alternatively be named as Man Made Vitreous Fibres (MMV fibres).

The health hazards which are associated with asbestos-containing products have resulted in a ban on the use of such products in new constructions and in the need to find environmentally acceptable ways of disposing of existing asbestos-containing products.

These problems are associated both with products having a very high content of asbestos fibre, such as asbestos insulation and other fibrous material and products having lower contents of asbestos such as asbestos cement products.

One way of attempting to dispose of asbestos-containing products is by dumping them at special sites under conditions such that asbestos fibres cannot subsequently escape, for instance by wrapping the products in plastic foil. This is particularly inconvenient for rigid, bulky products such as asbestos cement products.

There have been several proposals in the literature for rendering asbestos products harmless by heating the products.

In EP-A-344563 chrysotile asbestos is heated at a temperature of at least 580°C (eg. up to 650°C) so as to eliminate crystal-bonded water and convert the fibrous chrysotile asbestos into non-fibrous mineral forsterite.

In EP-A-265051 it is proposed to heat fibrous asbestos in an induction furnace at a temperature preferably between

1400 and 1500°C in the absence of any additives, and the melt is then discharged from the furnace and the product can be used in the ceramic or glass industries or as an adhesive or as a land fill. Although it is mentioned in
5 EP265051 that asbestos can occur as an asbestos cement product, normal asbestos cement has a melting point in the range 1800°C to 2000°C or more and so clearly asbestos cement cannot be used in the described process of EP-A-265051.

10 In DE-A-4211161 asbestos products are rendered harmless by heating in a non-aqueous system at a temperature of not more than 1300°C. The asbestos is subjected to the heating in the form of a blend with various additives. In some of the examples the asbestos is
15 introduced as asbestos fibre and the blend is stated to melt during the heating at below 1300°C. In other examples, the asbestos is introduced as a minor component (for instance 33 to 42% based on the dry weight) of a blend of asbestos cement and additives, and the heating is said
20 to result in sintering. The combination of the asbestos cement and the amount and type of additives would not cause melting at the exemplified temperatures (eg. 1000°C).

In US4820328 asbestos is converted into a glass by adding asbestos to a melt in an electric glass melting
25 furnace in a particular way, at a temperature of at least 1000°C. It is stated that the preferred temperature is 1350°C to 1380°C corresponding to a temperature of about 1250°C at the top of the molten glass.

Although it is stated that 100% blue asbestos can be
30 melted, preferably the asbestos is produced as a blend with glass cullet (waste glass) and usually also with caustic soda. In the examples, temperatures ranging from 1050°C to 1380°C are mentioned. It is stated that a blend of 78% asbestos and 22% cullet could be melted; the data in
35 example 1 clearly shows the need to use large amounts of cullet, and usually also caustic soda, if satisfactory melting is to be obtained in that example. Thus the

example shows that none of the blends that contain 50% asbestos or more provide a satisfactory melt. Instead, satisfactory melts are obtained only when asbestos is in an amount of 40% or less and caustic soda is present in an amount of at least 10%.

There is a reference in US4820328 to the fact that the asbestos that can be used in the invention can include asbestos cement materials. However it is clear that simple replacement of the asbestos fibre in the examples with asbestos cement would not be possible because asbestos cement has a melting point (1800°C to 2000°C or more) very much higher than any of the melting temperatures mentioned in U.S. 4,820,328.

Because of the very large amounts of asbestos cement boards, roofing, piping and other products that are having to be disposed of, there is an acute need of developing a cost effective and efficient way of rendering such products harmless, and which is more environmentally friendly than merely wrapping the asbestos cement in plastic and dumping it. No economic way has previously been proposed. As shown above, the literature is misleading in suggesting (erroneously) that it is possible to melt asbestos cement under conditions similar to those proposed for melting a charge consisting of asbestos fibre or asbestos fibre with glass.

Although melting asbestos cement by itself would, in theory, render it harmless, in practice this is not a viable process. The melting would require very high temperatures (at least 1800°C) and the melt would be highly corrosive because of the high calcium content of the asbestos cement. It is not practicable, in a cost effective process, to provide a furnace that can withstand this combination of temperature and corrosiveness.

An object of the invention therefore is to provide a cost effective method for rendering asbestos cement harmless and, in particular, to provide such a method that

yields a product that is economically useful and that, preferably, can be converted into MMV fibres.

Thus a particular object of the invention is to start with an environmentally unacceptable asbestos fibre product (asbestos cement) and to convert it into an environmentally acceptable MMV fibre product.

A process according to the invention for converting asbestos cement to a harmless product comprises heating in a furnace a blend of asbestos cement and additives, wherein at least 50% by weight of the additives is naturally occurring silicate material

the additives have a content of $\text{SiO}_2 + \text{Al}_2\text{O}_3$ which is at least 60% by weight of the additives,

the blend comprises 50 to 85% by weight asbestos cement and 15 to 50% by weight of the additives,

the blend of asbestos cement and the additives has a content of CaO of not more than 50% by weight of the blend,

the blend of asbestos cement and the additives is melted in the furnace by heating to a temperature between 1400°C and 1700°C at which the blend is molten, and

the molten blend is discharged from the furnace and is cooled and solidified.

The invention thus provides a very simple and economically cost effective way of disposing of asbestos cement and converting it to a harmless and useful product. Indeed, the process can be conducted in conventional electric and other furnaces having refractory linings that are convention for, for instance, the melting of mineral melts such as rock.

The additive has to be selected in accordance with the definition given above and additives such as those proposed in US4820328 are not suitable. For instance, if asbestos cement is blended with just sufficient glass cullet to reduce its melting point to, for instance, 1700°C, the resulting blend would have an unacceptably high CaO content and would be corrosive. If sufficient glass cullet and caustic soda is added to reduce the melting point of

typical asbestos cement to more convenient temperatures such as the 1350 to 1380°C range in U.S. 4,820,328 (or the temperatures used in the invention), the corrosiveness of the melt may become less of a problem but the amount of additives is so large (the asbestos cement constituting well under 50% (and often under 40%) of the blend) that the furnace and the amount of energy required for operating the furnace both become unacceptably large. Thus a large proportion of the total amount of energy merely goes into melting the additive, and much of this heat energy is wasted when the additive (as part of the final product) is discharged from the furnace and solidifies.

The asbestos cement products that can be treated in the invention can be any conventional asbestos cement products such as asbestos cement boards, pipes and roofing and comprise a cement matrix in which asbestos fibres are embedded, usually in an amount of 5 to 20% by weight of the product, typically around 10% by weight.

The asbestos cement is provided in the furnace as a blend with additives, either as a result of being mixed in the furnace or as a result of being pre-blended. The amount of the additives is about 15 to 50% by weight of the blend, most preferably around 20 to 40% by weight of the blend. Thus the asbestos cement is preferably 60 to 80% by weight of the blend.

The additives (ie. the total combination of additives) must have a high content of $\text{SiO}_2 + \text{Al}_2\text{O}_3$, which in practice is always at least 60%, usually at least 70%, by weight of the total additives. An alternative way of describing the total additives is to state that the additives have a low content of calcium oxide and a low content of alkali metal oxide. In practice the amount of CaO should be not more than 40% (usually below 30 and most usually below 20%) and the amount of $\text{Na}_2\text{O} + \text{K}_2\text{O}$ is not more than 20% and usually not more than 10% by weight of the additives.

At least 50% by weight of the additives and frequently more, for instance 60%, 70% or 80% and frequently

substantially all the additives, must be a silicate material which is selected to provide an optimum cost effectiveness to the blend.

5 This major component of the blend is naturally occurring silicate material. Such materials are cost effective as additives and it is possible, by review of the wide range of silicate materials that are naturally occurring, to select such materials which are cost effective and which, when used in economically acceptable
10 proportions, will result in a desired chemical composition and liquidous temperature of the blend.

The naturally occurring silicate material, and often at least 50%, or each component, in the additives may be a silicate material which has a very high content of SiO_2 + Al_2O_3 , usually at least 60 or 70% by weight and typically
15 at least 80% by weight, since the inclusion of such materials facilitates the attainment of a blend having a suitable liquidous temperature and the desired acceptably low CaO content while using relatively small amounts of
20 this particular additive.

Preferred naturally occurring silicate materials which can be used in the invention include quartz sand, sandstone, diabase, basalt, gabbro, pyroxenite, olivine sand, anorthosite, syenite, andesite, trachyte, diopside-
25 or wollastonite-rich rocks, clay and kaolin.

When referring above to naturally occurring silicate materials, we mean silicate materials that occur naturally in the environment and which either have not been used for other purposes prior to use in the invention or are
30 reclaimed materials that have been used for other purposes wherein these other purposes have not resulted in melting the additive prior to being used in the invention.

If a minor proportion of the additive is provided by materials which are neither naturally occurring silicate
35 materials nor the high (above 70%) SiO_2 + Al_2O_3 materials discussed above, these other additives and their amount should be selected having regard to the chemical analysis

and physical properties required for the final melt. They can include asbestos fibres themselves but more usually are selected from materials such as iron ore and waste materials such as acid slags, concrete, glass, tile, and MMV wool.

It is often preferred to use additives wherein at least 50% and preferably up to 100%, of the additives are relatively low melting point rock materials such as andesite and trachytes. In other systems it is preferred to use naturally occurring high SiO_2 products such as quartz sand or olivine sand, especially when low Al_2O_3 is preferred.

Since, for economic reasons, the melt temperature in the invention is maintained at not more 1700°C (and preferably 1400 to 1550°C) it is generally necessary that the blend of additives and asbestos cement should give a liquidous temperature of not more than 1600°C , preferably below 1450°C and most preferably below 1300°C . The liquidous temperature is the temperature at which the entire blend is just melted. Generally the melt temperature should be at least 100°C above the liquidus temperature.

Generally, the melt temperature is in the range 1400°C to 1700°C . Preferably, the melt temperature is between 1400 and 1550°C .

The blend of asbestos cement and additives must be such that the corrosiveness of the blend is acceptable for the furnace that is being used. In practice this generally means that the blend should have a CaO content of not more than 50%, preferably not more than 45%. The CaO content can be as low as possible, for instance below 30% in some blends.

The amount of $\text{SiO}_2 + \text{Al}_2\text{O}_3$ in the blend is usually at least 35% and preferably at least 45%, but is usually not more than 60% and preferably not more than 50%.

Preferably the blend of asbestos cement and additives is such that the blend, and therefore the melt, has a composition within the ranges

	SiO ₂	35-75% by weight
5	Al ₂ O ₃	2-45% by weight
	TiO ₂	0-10% by weight
	FeO	0-20% by weight
	CaO	10-50% by weight
	MgO	2-40% by weight
10	Na ₂ O	0-10% by weight
	K ₂ O	0-10% by weight
	Other oxides	0-20% by weight

In this specification, values quoted as FeO are intended to represent the total value of iron expressed as FeO, irrespective of the oxidation state of the iron.

These "other oxides" may be omitted but if they are present they may be for instance P₂O₅ and/or B₂O₃, generally each in an amount of not more than 10%, typically 5 - 10%. However any non-interfering element can be used, particularly if it has beneficial effects, such as improved solubility in lung fluids. The total amount of such additional elements is generally not more than 10 or 20%, calculated as oxides. Usually each such element is present in an amount of not more than 5 or 10%.

It will be understood by those skilled in the art that, for any particular blend, the proportions of components have to be selected (generally within the ranges quoted above) so as to obtain a blend having an appropriate liquidus temperature. In particular, it will be understood that not every possible combination of elements, within the ranges quoted above, will provide a blend having an appropriate liquidous temperature.

For instance suitable blends often have Al₂O₃+SiO₂ as much as 90% or more when the amount of Al₂O₃ is relatively low, but if the amount of Al₂O₃ is increased (eg, above 25%) it may be appropriate to reduce Al₂O₃+SiO₂ to around 60% in order to maintain a suitable liquidous temperature.

Preferred melts have a composition within the range

	SiO_2	35-66% by weight
	Al_2O_3	2-35% by weight
	TiO_2	0-10% by weight
5	FeO	0-10% by weight
	CaO	10-45% by weight
	MgO	2-30% by weight
	$\text{Na}_2\text{O} + \text{K}_2\text{O}$	0-7% by weight

but may additionally include P_2O_5 and for B_2O_3 and/or other
10 oxides generally in a total amount of not more than 20%.
Again, it is necessary, within these ranges, to select
proportions that give an appropriate blend, preferably with
a melt temperature in the range 1400 to 1550°C. This
particular combination of elements is particularly valuable
15 for the production of MMV fibres.

When the melt is to be used for the production of MMV
fibres it is generally preferred to minimise the amount of
alumina in the melt and so preferred blends have an alumina
content of below 10% and preferably below 4%. The
20 additives for the production of such a blend therefore
should have a very low alumina content and it is
particularly preferred that at least 50%, preferably at
least 80% and often substantially all, the additives are
quartz sand and olivine sand.

25 The furnace that is used for the process can be any
furnace provided with heating means adequate for generating
the required melt temperature and a lining that is
resistant to corrosion by the melt. Because, in the
invention, it is possible to formulate the melt so that it
30 has a corrosiveness typical of rock melts, lining
conventional for resisting rock melts can be used. The
furnace can therefore be a conventional cupola furnace but
is preferably a conventional lined electric furnace.

Although the solidified blend may subsequently be
35 remelted, especially if it is to be used for forming MMV
fibre material, it is preferred that this remelting should
be conducted in a different furnace at a different

location. In order to minimise environmental problems that are associated with handling asbestos cement, the furnace used for melting the asbestos cement products may be designed and positioned having particular regard to environmental considerations, and the solidified product from this furnace can then be used in conventional manner. Accordingly the furnace can be located close to the origin of the asbestos cement products that are to be destroyed and it is not essential in the invention to transport the asbestos cement products, possibly over long distances, to furnaces equipped for making MMV fibre material (although if desired MMV fibre material can be made direct from the melt).

The furnace for melting the asbestos cement is preferably provided with equipment for receiving closed containers, by which the asbestos cement products are transported to the furnace, and for achieving dust-free emptying of the transportation containers either direct into the furnace or direct into a store which in turn leads direct into the furnace. The additives that are to be incorporated with the asbestos cement in the furnace may be added separately into the furnace or may be added into the asbestos cement products before they are fed into the furnace.

A suitable furnace for use in the invention is capable of converting about 10 tons of asbestos cement material per production hour, and thus each plant conveniently can convert about 40,000 tons of asbestos cement waste products per year.

The melt can be discharged and solidified by a conventional MMV fiberising process, but is usually discharged and solidified as a bulk product such as a slab or block or brick. This can be used without further melting. For instance it can be used as an aggregate, e.g., for road surfaces. In order to promote its formation as an aggregate of sharp-edged grains it may be desirable to quench the molten blend.

Generally, however, the molten blend is solidified in the form of regular units, for instance by casting it in moulds to provide products which can be in the shape of plates or blocks. These plates, blocks or other regular units can then be used as part or all of the charge to a furnace that provides a melt by which synthetic mineral fibre material can be formed. Thus the moulded units can be transported to an existing plant for making synthetic mineral fibres and may be used as part or all of the charge in that plant. Typical plates or blocks have dimensions 50-250 x 100-250 x 100-250mm.

The moulded units or other solidified blend may be used alone or with raw materials conventionally used in the production of MMV fibres, and the resultant charge can be heated to form a melt and fiberised in conventional manner. For instance it can be heated in an electric furnace or, more usually, with coke in a cupola furnace. If the solidified blend has the chemical composition that is required for manufacture of the MMV fibres, then the solidified blend may be used as the sole mineral component of the fibre-forming melt, but more usually the solidified blend is used merely as a part, for instance at least 30%, of the mineral charge. The remainder may be conventional materials such as waste inorganic insulation material and conventional rock materials such as diabase, basalt, quartz sand, olivine sand, or slag materials.

It is particularly preferred that the MMV fibres should be soluble in lung liquids and for this purpose it is preferred that they should have a low content of Al_2O_3 , generally less than 4%. The additives used in the initial blend with asbestos cement, and any additives in the charge for forming the fibre product, should therefore be selected so that the fibres obtained from the final charge have an acceptable solubility in lung fluids. For this purpose it is particularly preferred that the additives used with the asbestos cement should have a low content of Al_2O_3 and preferably quartz sand and/or olivine sand is used as at

least half, and often more, of the total additives used in the total process. Suitable analyses of the melt, when solubility in lung fluid is required, are known from the literature, for instance Danish patent applications
 5 1566/92, and 1568/92. A content of P_2O_5 and/or B_2O_3 in amounts of up to 20%, generally in amounts of 5 - 10% of one or both, may be used for the manufacture of soluble MMV fibres. Typical analyses of suitable fibres are

	SiO_2	53.5-64% by weight
10	Al_2O_3	$\leq 4\%$ by weight
	CaO	10-20% by weight
	MgO	10-20% by weight
	FeO	6.5-9% by weight
	$P_2O_5 + B_2O_3$	0-20% by weight

15 Another analysis of suitable fibres is

	SiO_2	53.5-65% by weight
	Al_2O_3	$\leq 4\%$ by weight
	CaO	15-30% by weight
	MgO	5-15% by weight
20	FeO	$\leq 4\%$ by weight
	$P_2O_5 + B_2O_3$	0-20% by weight

In each of these analyses, there may additionally be minor amounts of other, non-harmful, elements. The amount of P_2O_5 is usually 0 - 10%, often 5 - 10%. The amount of
 25 B_2O_3 is usually 0 - 10%, often 5 - 10%.

A difficulty prior to the invention in the production of low Al_2O_3 -content mineral fibres has been that starting materials having a suitable low aluminium content are only available in limited amounts in nature, and therefore the
 30 costs associated with the production of the soluble fibres have been rather high. By the invention, it is possible to start from an environmentally harmful waste product and achieve fibres having low alumina content in an economically acceptable process. For instance the
 35 starting materials for the production of such fibres could be 50% asbestos cement, 37% quartz sand and 13% olivine sand.

When the MMV fibres are to be made from the initial melt obtained with the asbestos cement, the additives in the blend containing the asbestos cement must be selected such that the melt has the composition that is required for the MMV fibres. However if the fibre production is to be effected on the basis of a melt formed in a cupola furnace, it will, as mentioned above, be advantageous to initially produce plates or blocks from the above starting materials and then to use the plates or blocks for the charging of the cupola furnace, or by using plates or blocks having a higher content of converted asbestos cement in combination with other raw materials.

The molten charge may be converted into MMV fibre material by extrusion through a spinning cup or by pouring on to a spinner comprising at least two co-operating spinning wheels in conventional manner (for instance as described in U.S. 4,105,425 or WO92/06047).

The following are examples of the invention.

Example 1

Conventional MMV fibres

Crushed asbestos cement boards are admixed with quartz sand in the ratio of 80% of asbestos cement boards containing 10% of chrysotile asbestos to 20% of quartz.

The mixture is charged to an electrode-heated electric furnace and melted at 1550°C. The melt is moulded in the form of tiles in moulds with the dimensions 50 x 200 x 200mm.

The composition of the melt thus obtained is:

	SiO ₂	Al ₂ O ₃	TiO ₂	FeO	CaO	MgO	Na ₂ O	K ₂ O
30	45.2	3.3	0.3	1.5	43.3	4.8	0.2	0.5

The moulded tiles are used as raw material in a cupola furnace in the following charge:

40% of tiles (of the above composition)

60% of diabase

35 15% of coke

The following chemical composition was obtained:

	SiO ₂	Al ₂ O ₃	TiO ₂	FeO	CaO	MgO	Na ₂ O	K ₂ O
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44.4 10.3 1.6 6.5 20.1 8.9 2.1 0.9

The melt formed is converted into MMV fibres on a 4-wheel centrifugal spinner.

Example 2

5 Soluble MMV fibres

Crushed asbestos cement boards containing 10% of chrysotile fibres are mixed with quartz sand in the following charge:

25% of quartz sand to 75% of asbestos cement boards.

10 The mixture is charged to the electric furnace and melted at 1550°C.

The following chemical composition is obtained:

SiO ₂	Al ₂ O ₃	TiO ₂	FeO	CaO	MgO	Na ₂ O	K ₂ O
47.7	3.2	0.3	1.4	41.1	4.5	0.2	0.6

15 The moulded tiles are charged to a cupola furnace together with cement briquettes:

50% of tiles (of the above composition)

50% of cement briquettes

15% of coke

20 Cement briquette composition:

13% of cement

30% of quartz sand

51% of mineral wool waste

2% of olivine sand

25 4% of iron ore

The following MMV fibre composition is obtained:

SiO ₂	Al ₂ O ₃	TiO ₂	FeO	CaO	MgO	Na ₂ O	K ₂ O
56.4	3.5	0.3	2.4	28.2	7.1	0.5	0.7

30 The fibre material is formed by discharging the melt onto a 4-wheel spinner.

Example 3

When 100 t of an asbestos cement is converted into a melt using the additives described in US 4,820,328 for use with asbestos fibres, this requires the addition of 150 t of additives in the form of 135 t of waste glass and 15 t of soda and requires an amount of heat of 690 GJ. When 100t of similar asbestos cement is converted to a melt in

the invention, only 25 t of additives in the form of (quartz) sand need be used and the process requires only 385 GJ heat. Thus, in this example, the invention uses less than one fifth of the amount of additives and only slightly above half the amount of energy and can more easily be adapted to give low- Al_2O_3 fibres and a relatively non-corrosive melt.

CLAIMS

1. A process for converting asbestos cement to a harmless product comprising heating in a furnace a blend of asbestos cement and additives, characterised in that

5 at least 50% by weight of the additives is naturally occurring silicate material,

the additives have a content of $\text{SiO}_2 + \text{Al}_2\text{O}_3$ which is at least 60% by weight of the additives,

10 the blend comprises 50 to 85% by weight asbestos cement and 15 to 50% by weight of the additives,

the blend of asbestos cement and the additives has a content of CaO of not more than 50% by weight of the blend,

15 the blend of asbestos cement and the additives is melted in the furnace by heating to a temperature between 1400°C and 1700°C at which the blend is molten, and

the molten blend is discharged from the furnace and is cooled and solidified.

2. A process according to claim 1 in which the blend of asbestos cement and additives has a composition within the
20 ranges

SiO_2	35-75% by weight
Al_2O_3	2-45% by weight
TiO_2	0-10% by weight
FeO	0-20% by weight
25 CaO	10-50% by weight
MgO	2-40% by weight
Na_2O	0-10% by weight
K_2O	0-10% by weight
Other oxides	0-20% by weight

30 3. A process according to claim 1 in which the blend of asbestos cement and additives has a composition within the range

SiO_2	35-66% by weight
Al_2O_3	2-35% by weight
35 TiO_2	0-10% by weight
FeO	0-10% by weight
CaO	10-45% by weight

MgO	2-30% by weight
Na ₂ O + K ₂ O	0-7% by weight
Other oxides	0-20% by weight

4. A process according to any preceding claim in which
5 the blend is formed of 60 to 80% asbestos cement and 20 to 40% additives of.
5. A process according to any preceding claim in which at least 80% by weight of the additives is naturally occurring silicate material.
- 10 6. A process according to any preceding claim in which the naturally occurring silicate is selected from the group consisting of quartz sand, sandstone, diabase, basalt, gabbro, pyroxenite, olivine sand, anorthosite, syenite, andesite, trachyte, diopside- or wollastonite- rich rocks,
15 clay and kaolin.
7. A process according to any preceding claim in which substantially all the additives are selected from quartz sand and olivine sand.
8. A process according to any preceding claim in which at
20 least 50% by weight of the additives have a content of SiO₂+Al₂O₃ of at least 70% by weight.
9. A process according to any preceding claim in which the additives and their amount are selected such that the blend has a liquidus temperature of not more than 1600°C.
- 25 10. A process according to any preceding claim in which the temperature of the melt is 1400 to 1550°C.
11. A process according to any preceding claim in which the molten blend is cast into regular units or is quenched and fractured into grains or is formed into man made
30 vitreous fibre material.
12. A process according to any preceding claim for forming man made vitreous fibre material, comprising forming a melt from a charge comprising the solidified blend, and forming the fibre material from the melt.
- 35 13. A process according to claim 11 or claim 12 for forming man made vitreous fibre material in which the fibre material has a content of Al₂O₃ of below 4%.

14. A process according to claim 13 in which the fibre material has the composition

	SiO_2	53.5-64% by weight
	Al_2O_3	$\leq 4\%$ by weight
5	CaO	10-20% by weight
	MgO	10-20% by weight
	FeO	6.5-9% by weight
	$\text{P}_2\text{O}_5 + \text{B}_2\text{O}_3$	0-20% by weight

15. A process according to claim 13 in which the charge has the composition

10	SiO_2	53.5-65% by weight
	Al_2O_3	$\leq 4\%$ by weight
	CaO	15-30% by weight
	MgO	5-15% by weight
15	FeO	$\leq 4\%$ by weight
	$\text{P}_2\text{O}_5 + \text{B}_2\text{O}_3$	0-20% by weight

INTERNATIONAL SEARCH REPORT

Inter- national Application No.
PCT/EP 94/01215

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 A62D3/00 C04B20/02 B09B3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 A62D C04B B09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	DE,A,42 11 161 (KERAMIT) 7 October 1993 cited in the application see examples ---	1-15
P,X	EP,A,0 568 367 (THE DOW CHEMICAL COMPANY) 3 November 1993 see column 6, line 25-29 see column 9; example 3 ---	1
A	Week 9106, Derwent Publications Ltd., London, GB; AN 91-040582 & JP,A,2 307 836 (SUMITOMO METAL IND KK) 21 December 1990 see abstract ---	1,6
A	WO,A,91 00123 (R.B. EK) 10 January 1991 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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- "P" document published prior to the international filing date but later than the priority date claimed

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- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search

18 August 1994

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No.

PCT/EP 94/01215

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		AU-A- 6038990	17-01-91
		CA-A- 2063386	30-12-90
		EP-A- 0479894	15-04-92
		US-A- 5096692	17-03-92